Flame and Temperature Measurement Using Vibrational Spectroscopy

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Abstract

An overview of the application of vibrational spectroscopy to the study of flames is provided. The mathematics of interpretation of flame spectra for determination of species concentration and temperature are introduced. The history of the application of vibrational spectroscopy to the study of flames is briefly summarized. Applications of methods using dispersive absorption and emission spectroscopy and of methods using tunable diode lasers (TDLs) to the study of flame systems are discussed.

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1. Introduction

The application of modern spectroscopic analysis to the study of flames began in the 1920s and 1930s with breakthroughs in the understanding of atomic and molecular spectroscopy (Gaydon 1948). The earliest spectroscopic investigations focused on understanding the line and band structure observed in the visible and ultraviolet (UV) regions of the spectrum when the light from the flame was dispersed by a grating or prism. One of the great breakthroughs of physics during this period was the understanding that the band structure observed in the emission spectra of flames originated from gas phase molecular species (Hertzberg 1950a).

For molecular species, understanding the appearance of flame spectra is simplified by assuming that the total internal energy, E_T, of a gas phase molecule may be given to first order (Born-Oppenheimer approximation) as

$$E_T = E_{EL} + E_{VIB} + E_{ROT}. \tag{1}$$

Here, E_{EL}, E_{VIB}, and E_{ROT} are, respectively, the quantized electronic, vibrational, and rotational energy of the molecular species. In the scientific literature, these energies are usually expressed in terms of wave numbers (the reciprocal wavelength, expressed in centimeters, which is directly proportional to energy, and given the symbol cm^{-1}). All observed spectral features, in emission and absorption, are caused by changes in total energy, ΔE_T, of the individual species present within the flame. Spectral features arise from the emission or absorption of a photon with energy corresponding to the difference between initial and final states of the transition. Figure 1 illustrates the absorption of a photon corresponding to an electronic transition (Figure 1[a]) and to a vibrational transition (Figure 1[b]) for a diatomic molecule whose interatomic potential energy may be approximated by an an harmonic oscillator (Hertzberg 1950a).

In general, changes in electronic, vibrational, and rotational energy correspond to emission or absorption of radiation in the visible (and UV), infrared (IR), and microwave region of the electromagnetic spectrum, respectively. Typically, $\Delta E_{EL} > \Delta E_{VIB} > \Delta E_{ROT}$. Molecular changes

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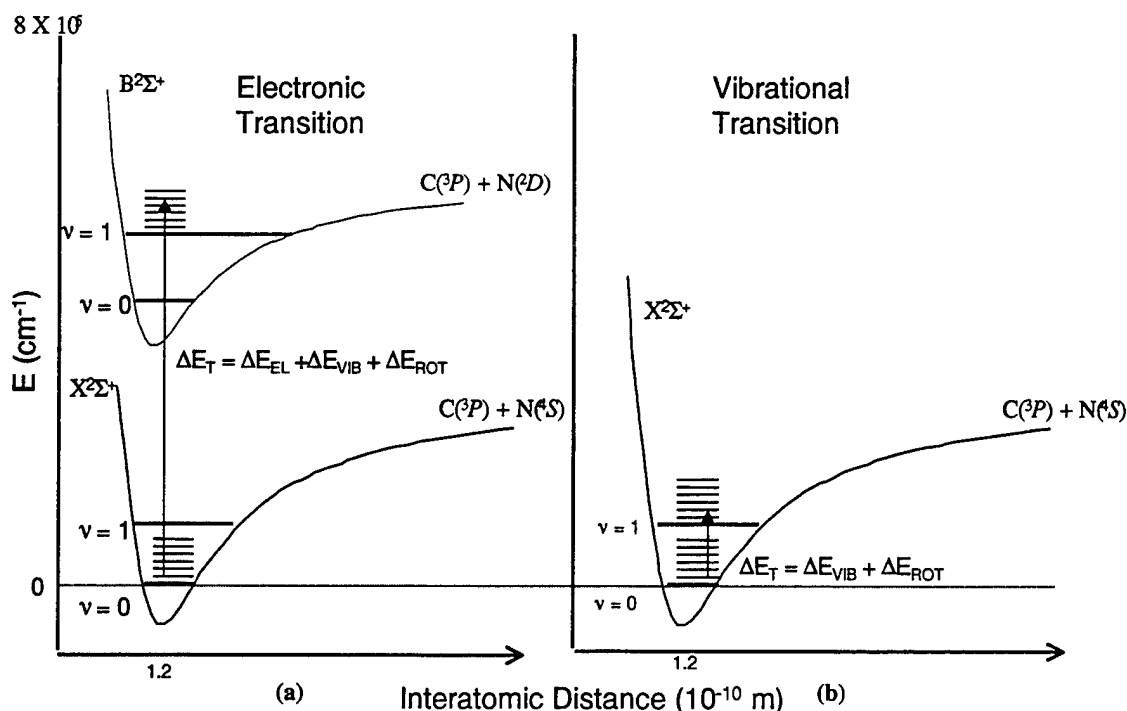
Figure 1. Potential Energy Diagram for a Diatomic Anharmonic Oscillator. Electronic (a) and Vibrational (b) Absorption Transitions Are Illustrated. Values for Interatomic Distance, Energy (E), and Term Symbols Are for the Radical Flame Species CN.

in E_{EL} are generally accompanied by changes in E_{VIB} and E_{ROT}, and changes in E_{VIB} may be (and almost always are) accompanied by changes in E_{ROT}. These general trends are illustrated in Figure 1. The band structure observed in the visible and UV spectra of molecular species in flames, emission, and absorption is therefore understood to be the result of combined changes in electronic, vibrational, and rotational energies (Hertzberg 1950b).

The visible and UV radiation from most flames usually accounts for less than 1% of the total emitted energy (Gaydon and Wolfhard 1953), with most of the energy emitted by a flame occurring in the IR region of the spectrum. To see why this is not unexpected, it is useful to compare the radiation emitted by a flame with the radiation emitted by a blackbody. In a system at thermodynamic equilibrium (which, on a macroscopic scale, a flame is not), the distribution of radiation is given by Planck's blackbody radiation law (Penner 1959):

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$$I_\lambda = [2E_\lambda c_1 \lambda^{-5}/(e^{c2/\lambda T} - 1)] \, Ad\lambda. \tag{2}$$

Here, I_λ is the wavelength-dependent radiant intensity normal to the surface of the radiator, E_λ is the emissivity at wavelength λ, c_1 and c_2 are the first and second radiation constants and have the values 0.588×10^{-8} W/m^2 and 1.438×10^{-2} m/K, respectively, T is temperature in Kelvin (K), and A is the area of the surface in square meters (m^2).

Figure 2 is a plot of equation (2) at several temperatures. Figure 2 shows that, for a blackbody radiator at temperatures up to 2,300 K, the peak spectral radiancy always occurs in the IR region of the spectrum. As the temperature increases above 2,300 K, the peak of spectral radiancy moves to shorter wavelengths (toward the visible region of the spectrum). It is important to note that, for a blackbody, the value of E_λ is equal to 1 at all wavelengths. In flames, the value of E_λ varies (and may approach 1) with wavelength, but is near 0 for most wavelengths, indicating that a flame is not a blackbody and that flame gases may not be in thermodynamic equilibrium. Nevertheless, in some cases where the emissivity of a flame species is known, measurements of spectral radiancy of flames may be used to calculate flame temperatures to within an accuracy of several Kelvin (Gaydon 1974).

When the regions of nonzero emissivity ($E_\lambda > 0$) in the flame emission spectrum are expanded along the wavelength scale, these regions exhibit detailed fine structure. In the visible and UV regions of the flame emission spectrum (in general, radiation with a wavelength between 1 μm and 200 nm), this fine structure represents changes in rotational and vibrational energy, which accompany changes in electronic energy. In the more intense IR region of the flame emission spectrum (in general, radiation with a wavelength between 1 and 30 μm), the observed fine structure is caused by transitions between rotational energy levels that occur with a change in vibrational energy but with no change in electronic energy. The amount by which the vibrational and rotational energies may change during a transition is governed by selection rules, which are largely dependent upon the symmetry of the species involved in the transition (Wilson et al. 1955).
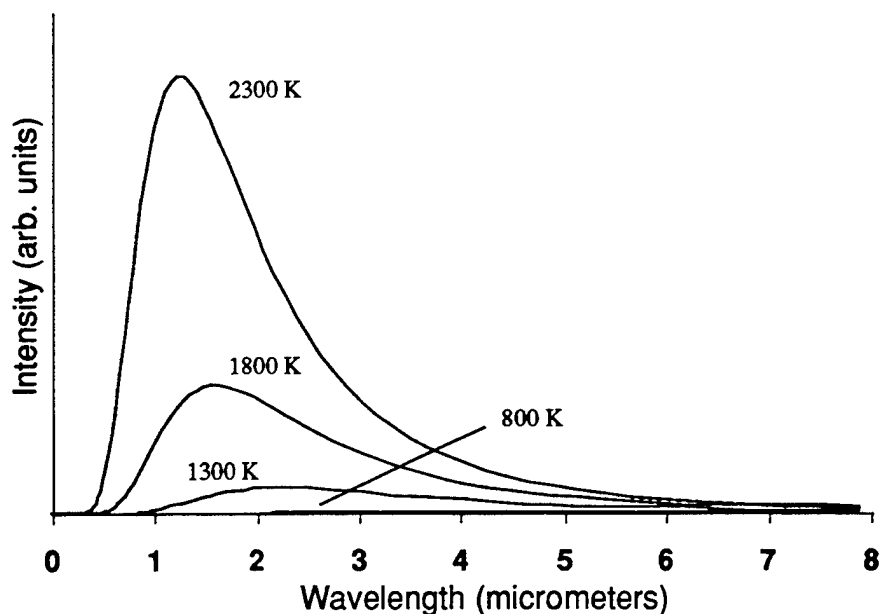
Figure 2. Radiation From an Ideal Blackbody at Several Temperatures.

Figure 3 shows the raw emission spectrum from a premixed, reduced pressure (18 torr) stoichiometric CH_4/O_2 flame measured using a Fourier-transform infrared (FTIR) spectrometer (McNesby et al. 1996) and the calculated emission from a blackbody at 1,173 K over the same spectral region. The peak temperature in this flame was measured (using a fine wire Pt-Pt/10%Rh thermocouple) to be near 2,150 K. Comparison of flame emission spectra to calculated blackbody radiance must take into account the emissivity of the different species within the flame, reabsorption of emitted radiation by cold gases outside of the flame region, emission from species at different temperatures along the line of sight of the measurement, chemiluminescence, and the variation in sensitivity of the instrument detector with wavelength. Figure 3 illustrates that care must be taken when estimating flame temperatures from measured spectra, since results from simple fits of a blackbody radiation curve to a measured spectrum may be inaccurate.

2. Background

Emission and absorption spectra of flames may be continuous or banded. Continuous emission spectra may be modeled using the Planck blackbody equation (equation [2]). Modeling

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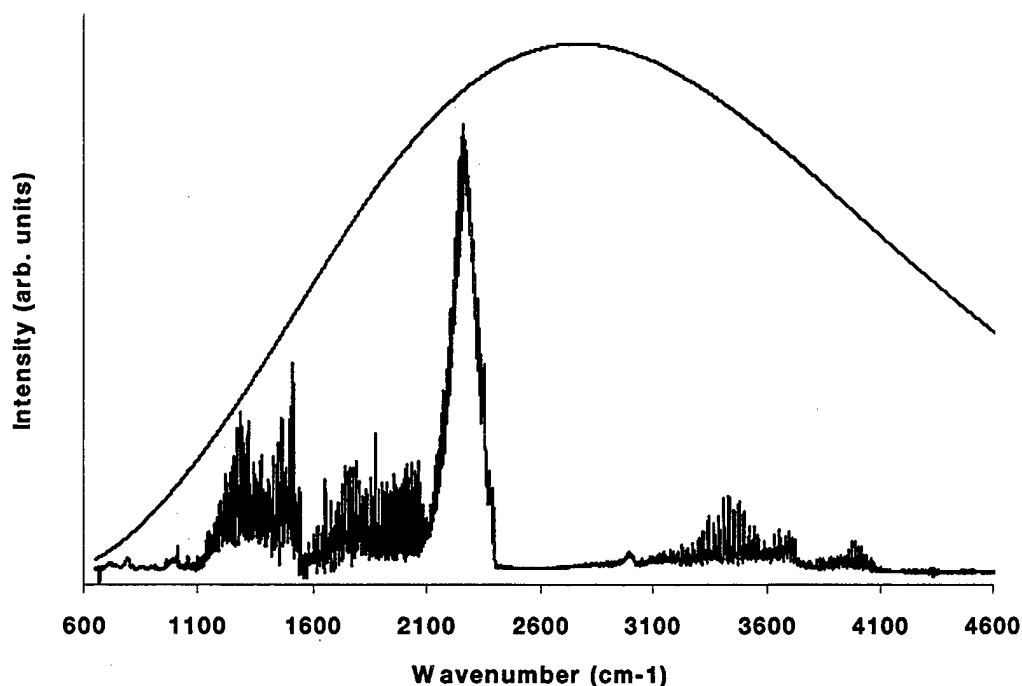
Figure 3. The IR Emission Spectrum Measured Using an FTIR Spectrometer From an 18-Torr CH_4/O_2 Flame and the Blackbody Radiation (1,173 K) Emitted Over the Same Region. The IR Emission Spectrum Has Not Been Correct for the Responsivity of the Detector.

of banded spectra requires an understanding of the statistics that govern the way the population of a species is distributed among available energy levels. It is the dependence of population of molecular energy levels upon temperature, and the influence of this population upon band shape and spectral emissivity and absorption, that makes vibrational spectroscopy a useful tool for flame diagnostics.

The necessary mathematics for species and temperature measurements from IR spectra of flames are outlined next. The example given is for a diatomic molecule, such as CO. It is assumed that the spectra are measured in absorption at low pressure, where the amount of light absorbed is less than approximately 5% of the incident intensity (often referred to as absorption in an optically thin medium). For extension to more complicated molecules (including more complicated diatomic molecules, such as NO) and to higher pressures, the reader should consult the texts referenced in the following sections.

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2.1 Population Distribution Among Available Energy Levels. The classical Maxwell-Boltzmann distribution law may be used to approximate the distribution of population among the quantized energy levels of a gas phase diatomic molecule (Hertzberg 1950a). For most diatomic molecules (such as CO but not NO), each separate lineshape observed in the infrared spectrum corresponds to a simultaneous change in vibrational and rotational energy. For this reason, the spectral lines that make up the band structure observed in most IR spectra are often called rovibrational transitions. For purposes here, it is convenient to describe the initial and final energy levels of the transition as rovibrational energy levels.

When describing two energy levels of a given species, the superscript ' denotes the state of higher energy and the superscript " denotes the state of lower energy. At thermodynamic equilibrium, the ratio of the number of molecules in the rovibrational energy level with vibrational quantum number v' and rotational quantum number J' to the number of molecules in the rovibrational energy level with vibrational quantum number v'' and rotational quantum number J'' is given by

$$N_{J'v'}/N_{J'',v''} = [(2J'+1)/(2J''+1)]\exp(-(\Delta E_v + \Delta E_J))hc/kT), \qquad (3)$$

where $N_{J'v'}$ is the population of the higher rovibrational energy level; $N_{J'',v''}$ is the population of the lower rovibrational energy level; ΔE_v is the change in vibrational energy (units of cm^{-1}); ΔE_J is the change in rotational energy (units of cm^{-1}), which occurs during the transition; h is Planck's constant; k is Boltzmann's constant; and c is the speed of light. The quantity $[(2J'+1)/(2J''+1)]$ accounts for the degeneracy of rotational levels for a given value of J, providing a statistical weight to the levels with a given rotational energy.

For interpretation of measured spectra, it is useful to know the fraction of the total population (N_T) in the energy level from which the transition originates. For absorption (where the transition originates from the level of lower energy), this may be given by

$$N_{J'',v''}/N_T = (N_{J'v'}/N_{J=0,v=0})/(\Sigma\, N_{Jv}/N_{J=0,v=0}), \qquad (4)$$

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where the summation is over all values of J" and v" and $N_{J=0,v=0}$ is the population in the rovibrational energy level with rotational quantum number J and vibrational quantum number v both equal to 0. The denominator on the right side of equation (4) may be written to a first approximation as

$$\Sigma \, N_{Jv}/N_{J=0,v=0} = \Sigma(2J + 1)\exp(-(E_v + BJ(J + 1))hc/kT). \tag{5}$$

The first rotational constant, B, is inversely proportional to the moment of inertia of the rotating molecule and determines the rotational energy level spacing. This means that, in general, the larger the mass of the rotating molecule, the closer is the spacing of the rotational energy levels. The right side of equation (5) may be factored into rotational and vibrational components:

$$\Sigma \, N_{J''v''}/N_{J=0,v=0} = Q_R Q_V, \tag{6}$$

where Q_R and Q_V are, respectively, the rotational partition function and the vibrational partition function:

$$Q_R = \Sigma(2J'' + 1)\exp(-B''J''(J'' + 1))hc/kT), \tag{7}$$

and

$$Q_V = \Sigma\exp(-E_{v''})hc/kT). \tag{8}$$

The summations in equations (7) and (8) are over all J and all v, respectively. Substituting equations (3), (7), and (8) into equation (4) gives

$$N_{J'',v''}/N_T = (2J'' + 1)\exp(-(E_{v''} + B''J''(J'' + 1))hc/kT)/Q_R Q_V. \tag{9}$$

Equation (9) shows how the fraction of total population in a given rovibrational energy level varies with temperature and rotational and vibrational quantum number. For most gas-phase

diatomic molecules, if the population in a known rovibrational level is measured, equation (9) allows the total population (and hence total pressure) of the gas to be calculated.

2.2 Absorption of Radiation. The Einstein transition probability of absorption, B_{mn}, (not to be confused with the first rotational constant, B) predicts the energy removed (IR) from an incident beam of radiation by an optically thin layer of absorbers for a transition from a lower state, m, to an upper state, n, as (Steinfeld 1974):

$$I_R = I_0 N_m B_{mn} \Delta x h V_{mn}, \tag{10}$$

where N_m is the number of molecules per unit volume in the energy level from which absorption occurs, I_0 is the energy crossing unit area of absorbers per second, Δx is the absorber thickness, and V_{mn} is the energy (in cm^{-1}) of the monochromatic radiation exciting the transition. In equation (10), $I_0 N_m B_{mn}$ is proportional to the number of transitions per second per unit volume produced by the radiation and hV_{mn} is proportional to the energy removed from the incident beam per transition (Hertzberg 1950a).

In an absorption experiment, the intensity of radiation exiting the absorbing medium, I, is described according to the Bouguer-Lambert Law (later restated by Beer for solutions [Moore 1972]):

$$I = I_0 \exp(-\sigma(\lambda)N_m x), \tag{11}$$

where x is the path length traveled by the light through the absorbing medium and $\sigma(\lambda)$ is called the cross section for absorption. This cross section represents the "effective area" that a molecule presents to the incident photons (Bernath 1995). When $\sigma(\lambda)N_m x$ is small (optically thin medium), equation (11) may be rewritten:

$$I_0 - I = I_0(\sigma(\lambda)N_m x). \tag{12}$$

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Integrating equation (12) over the wavelength range for which the absorption may occur gives

$$\int (I_0(\lambda) - I(\lambda))\, d\lambda = \int I_0(\lambda)(\sigma(\lambda)N_m x)\, d\lambda. \tag{13}$$

The way in which the cross section for absorption ($\sigma(\lambda)$) varies with wavelength depends mainly upon the total pressure of the gas (Townes and Schawlow 1955). For gas pressures above approximately 100 torr, the absorption is observed to occur with a Lorentzian lineshape (Anderson and Griffiths 1975) given by

$$\sigma(\lambda)N_m x = 2.303 A_0 \gamma^2/((c/\lambda - c/\lambda_0)^2 + \gamma^2), \tag{14}$$

where A_0 is the peak spectral Absorbance ($-\log(I(\lambda)/I_0(\lambda))$) at the wavelength of maximum light attenuation by the gas and γ is the half width at half height (HWHH) of the spectral line.

Substituting equation (14) into equation (13), assuming that I_0 is invariant with wavelength over the absorption linewidth and integrating over the full linewidth, gives

$$\int (I_0(\lambda) - I(\lambda))\, d\lambda = 2.303 I_0(\lambda) \int A_0 \gamma^2/((c/\lambda - c/\lambda_0)^2 + \gamma^2)\, d\lambda = 2.303 I_0(\lambda) \pi A_0 \gamma. \tag{15}$$

Substituting equation (15) into equation (10) and solving for the peak absorbance, A_0, gives

$$A_0 = N_m \Delta x\, B_{mn} h \nu_{mn}/2.303 \pi \gamma. \tag{16}$$

The number of molecules in the initial state, N_m, is related to the total number of molecules, N_T, through the vibrational (Q_v) and rotational (Q_r) partition functions:

$$N_m = N_T(2J'' + 1)\exp(-(E_{v''} + B''J''(J'' + 1))hc/kT)/Q_r Q_v. \tag{17}$$

Substituting equation (17) into equation (16) gives

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$$A_0 = [\Delta x \ B_{mn} h v_{mn} N_T (2J" + 1) / 2.303 \pi \gamma \ Q_r Q_v] \exp(-(E_{v"} + B"J"(J" + 1))hc/kT). \qquad (18)$$

Equation (18) is useful for extracting temperature and concentration information from measured values of peak absorbance (A_0) for individual transitions in a rovibrational band. By simultaneously fitting T and N_T to A_0 measured over a rovibrational band, temperature and gas pressure may be obtained. Equation (18) shows that it is necessary to know the HWHH of each line in the spectrum used in the calculation, and the value of B_{mn}. This is not always trivial, since this value may be temperature and J-value dependent. Additionally, it is important to recognize that peak absorbances must be corrected when measured with an instrument of moderate spectral resolution. The method for extracting true peak absorbance from peak absorbance measured at moderate resolution has been treated in detail by Anderson and Griffiths (1977).

Substituting equation (18) into equation (16) and expressing the result in the form of the Bouguer-Lambert Law (equation [11]) gives

$$I(\lambda)/I_0(\lambda) = \exp[(-\Delta x \ B_{mn} h v_{mn}(\lambda) N_T \gamma / (\pi Q_r Q_v ((c/\lambda - c/\lambda_0)^2 + \gamma^2))$$

$$\times (2J" + 1)\exp(-(E_{v"} + B"J"(J" + 1))hc/kT)]. \qquad (19)$$

Equation (19) allows direct comparison between high-resolution measurements of transmittance $(I(\lambda)/I_0(\lambda))$ and transmittance calculated from spectral parameters, pressure of the absorbing gas, and the temperature. It should be noted that knowledge of the spectral line HWHH (γ) is required, as well as an instrument capable of measuring the transmittance at high resolution. In practice, values of B_{mn} (usually converted to linestrengths) for different rovibrational transitions are taken from the literature or estimated from measurements of total band strength (Varghese and Hanson 1980). Also, the Voight lineshape profile, which describes the convolution of a Gaussian lineshape function (applicable to gases at low pressure) and a Lorentzian lineshape function, is usually used to model spectral lines in flames at reduced pressure (Daniel et al. 1996). As with fits to data based upon equation (18), when spectra are measured on an instrument of moderate resolution (in general, an instrument resolution $> 0.1\gamma$),

the instrument lineshape function is convoluted with the true lineshape (equation [19]). When this is the case, this convolution must be included in the model (Vanderhoff et al. 1997).

Equation (19) describes the fully resolved band structure observed in high-resolution IR spectra of many gas phase diatomic molecules, such as CO. Figure 4 shows the transmittance $(I(\lambda)/I_0(\lambda))$ spectrum of CO, calculated using equation (19), for a constant number of molecules at the temperatures shown in Figure 2. Figure 4 shows that, as the temperature increases and more rotational energy levels become populated, the overall shape of the absorption band broadens to cover a wider spectral range. Additionally, because the total number of molecules is divided between a greater number of initial energy levels as temperature is increased, the intensity of individual rovibrational transitions changes with increasing temperature.

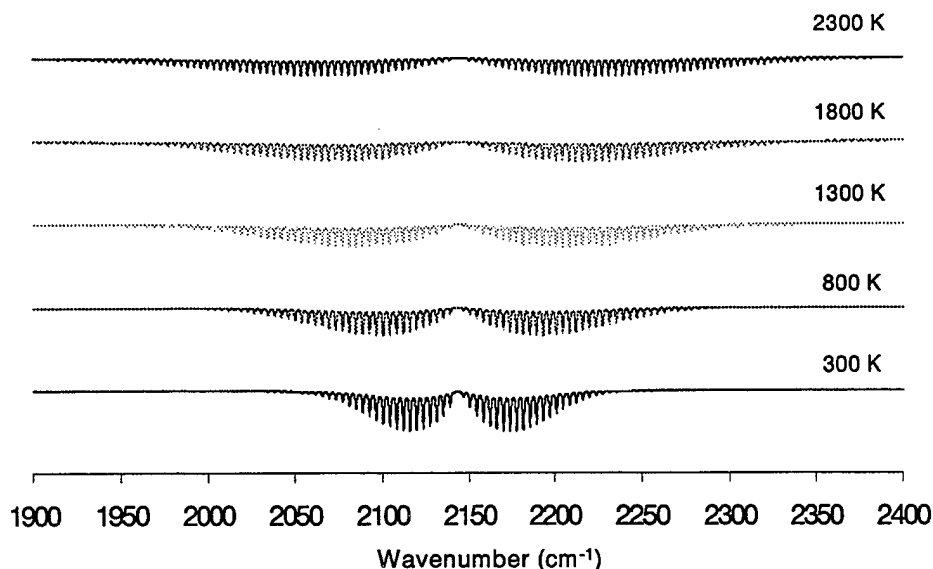**Figure 4. Calculated Transmittance of Light Through A Fixed Pressure of CO Gas at Different Temperatures. Spectra Are Offset for Clarity (Each Baseline Corresponds to 100% Transmission).**

3. Experimental Methods - Narrative

By the 1950s, the mathematical and instrumental methods for determination of temperatures and species concentrations from measurements of IR spectra had been established (Barnes 1977),

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in large part spurred by electronics developed during the second world war, by perfection of the method of commercial replication of diffraction gratings, and by publication in 1945 of Hertzbergs book *Infrared and Raman Spectra of Polyatomic Molecules* (Hertzberg 1950b). During the 1950s, comparison of IR emission spectra from high-temperature sources in different laboratories was complicated by temperature gradients along the measurement line of sight and by incomplete spectral parameters for gas absorption at high temperatures. To obtain spectral parameters for gases under study, several efforts were made to study gases in closed cells at controlled temperatures (Oppenheim 1963). Most of these efforts on studying gases at high temperature under static conditions employed absorption spectroscopy, in part to minimize self absorption along the line of sight and also to enable using modulation of the source radiation (allowing discrimination of the high-intensity, unmodulated background IR emission). The success in fundamental studies of band structure and in predicting emissivities and changes in absorption at high temperatures and pressures led to an increase, by the early 1960s, in studies of radiation transfer for systems ranging from jet and rocket motors to high-efficiency oil burners. A particular success that resulted from the study of gas phase emissivities was the determination of thermal stress on NASA rocket motors from exhaust gas radiation (Limbaugh 1985).

With the development in the early 1970s of the Fourier-transform spectrometer and the computer-based fast Fourier transform (FFT), it became possible to achieve high resolution coupled with high-energy throughput and phase-sensitive detection (Griffiths and de Haseth 1986). However, the development of laser-based techniques (particularly laser-induced fluorescence [LIF]) for measurement of flame radical species (such as OH, HCO, H, O, CH, and C_2) enabling direct measurement of species participating in flame propagation reactions (Daily 1997) caused a shift in focus of fundamental spectroscopic investigations of flame systems. This shift led to a decrease in the late 1960s and early 1970s in the number of publications describing basic research that applied the techniques of dispersive IR absorption and emission spectroscopy to flames.[*] This decrease was offset by a considerable body of work on emission studies of hot gas sources, particularly smokestack and waste gas plumes from industrial sources (Wormhoudt and Conant 1985).

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[*] This conclusion is based upon an informal survey of the *Proceedings of the International Symposia (International) on Combustion* published by Academic Press, from 1948 to 1996.

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By the late 1970s, laser based techniques employing tunable infrared lasers began to be used for species measurements in flames (Hanson et al. 1980). The majority of this work used tunable diode lasers (TDLs), semiconductor devices in which the output laser radiation wavelength is tuned by varying the temperature and diode injection current. Initial experiments used TDL's emitting narrow linewidth (typically < 10^{-4} cm^{-1}) radiation in the mid-infrared spectral region. The narrow linewidth usually enables species specificity, even in congested spectral regions. Since the laser linewidth is typically several orders of magnitude less than the absorption linewidth, measurements of the fully resolved absorption transition may be made, enabling the determination of lineshape dependence upon pressure and temperature. An additional advantage to using tunable diode lasers, besides very narrow linewidths, is the ability to tune the lasers rapidly (kHz to MHz) over their output wavelength range. This enables phase sensitive detection that minimizes the effect of the laser output noise, and also enables time resolved measurements of dynamic systems.

Recently, tunable diode lasers operating in the near-infrared spectral region have begun to see application to the spectroscopy of flames and to flame gases (Bomse et al. 1992; Silver 1992). At this time, commercial availability of TDLs in the mid-IR spectral range is greater than for the near-IR spectral range. TDLs operating in the mid-IR spectral range must be cooled to cryogenic temperatures. TDLs operating in the near-IR spectral range operate near room temperature, and, unlike mid-IR radiation, the near-IR radiation may be transmitted over long distances through optical fibers. However, since absorption in the near-IR spectral region corresponds to a change in vibrational quantum number greater than unity (referred to as an overtone transition), the sensitivity to a given molecule is much less than for mid-IR spectroscopy, which is usually used to measure rovibrational transitions in the fundamental vibrational band. Typically, mid-IR TDLs are used when extreme sensitivity is required (ppb range). For many field-based techniques that require transportability in rugged environments, near-IR TDLs are more appropriate (ppm range).

4. Experimental Methods - Dispersive and Fourier-Transform Spectroscopy

4.1 Emission Measurements. Since the mid-1970s, most measurements of emission spectra of steady flames have used Fourier-transform techniques. Figure 5 shows the emission spectrum measured from a premixed, stoichiometric CH_4/O_2 flame (total pressure equal to 18 torr) to which 3% CF_3Br has been added as a flame suppressant. When appropriate, reduced pressure flames are often studied because, at reduced pressure, the flame region is expanded, allowing more detailed study. The emission spectrum shown in Figure 5 was measured using an FTIR spectrometer at a resolution of 1 cm^{-1}.
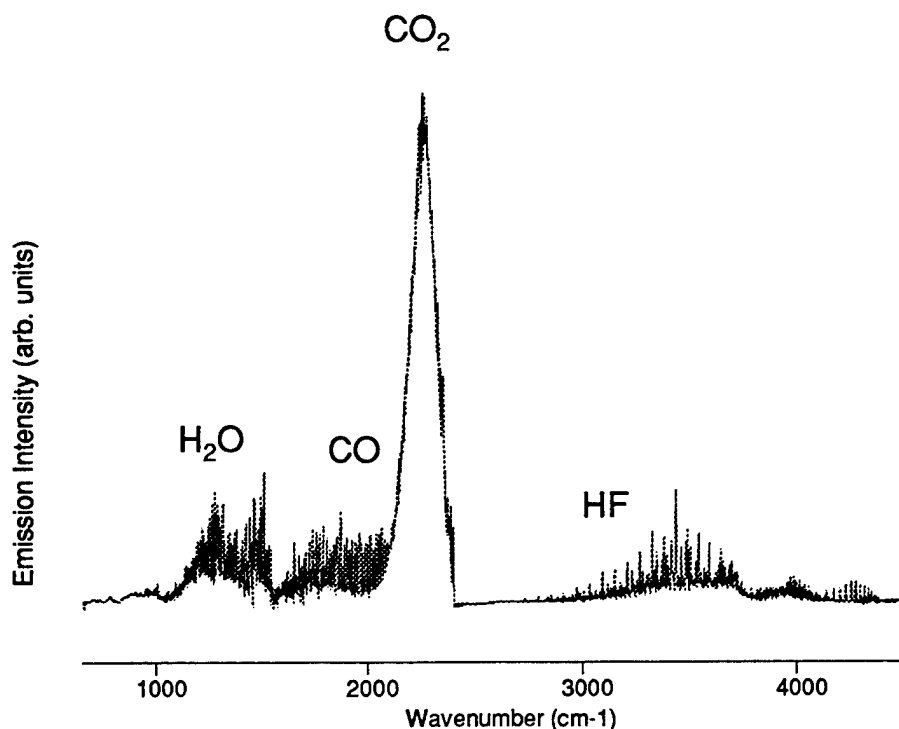
Figure 5. The IR Emission Spectrum Measured From a Premixed, Stoichiometric CH_4/O_2 Flame (Total Pressure 17 Torr) to Which 3% CF_3Br Has Been Added.

In Figure 5, spectral features from several flame species are identified, but the spectrum is dominated by emission from CO_2 and gaseous H_2O. This is because higher temperatures allow emission over a wide range of rovibrational transitions (see Figure 4) from combinations of

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different vibrational states and the geometry of the emitting species (specifically, in this case, H_2O) causes the spectrum to be complicated (relative to that for a diatomic molecule). The measured spectrum in Figure 5 reports emission from species over a wide range of temperatures because the line of sight from the flame center to the detector includes gases at many different temperatures. Also, because many flame species are products of an ongoing chemical reaction (combustion), these species may be produced with vibrational and rotational population distributions that are not in equilibrium with translational temperatures (Gaydon 1948). Because of this, temperatures calculated from emission spectra using expressions similar to equations (18) or (19) may give misleading results. When these factors are taken into account, temperature and partial pressures of gas species may be extracted from high-resolution measurements of IR-emission spectra (Wormhoudt and Conant 1985).

4.2 Absorption Measurements. Figure 6 shows an absorption spectrum measured through an opposed-flow CH_4/air flame (total pressure 50 torr) using a FTIR spectrometer at 1 cm^{-1} resolution. It should be noted that this spectrum is less congested and has a slightly more regular appearance than that shown in Figure 5. Absorption features from several species are evident in the spectrum. For flame diagnostics using IR-absorption spectroscopy, CO is probably the most widely studied molecule. The fundamental rovibrational absorption band of CO ($v = 0 - 1$, centered at 2,170 cm^{-1}) is well approximated by equation (19) and has a spacing between rotational lines (2B) of approximately 3.6 cm^{-1}. Modeling of measured spectra is relatively straightforward, and fully resolved rovibrational lines may be measured at moderate instrument resolution (although the reported lineshape may be just the instrument lineshape function [Anderson and Griffiths 1975]). In addition, since CO is a major product of hydrocarbon combustion, it is present in most flame systems. Figure 7 shows the spectrum of the first overtone ($v = 0 - 2$) of CO, measured using a dispersive system, and the fit to the measured spectrum using an equation similar to equation (19). Since the resolution of the spectrometer used to measure the spectrum in Figure 7 was insufficient to fully resolve the lineshapes of the individual rovibrational transitions, it was necessary to convolute the instrument function with the true lineshape function (equation [19]) to obtain an accurate fit of the measured to calculated spectrum (Vanderhoff et al. 1997).
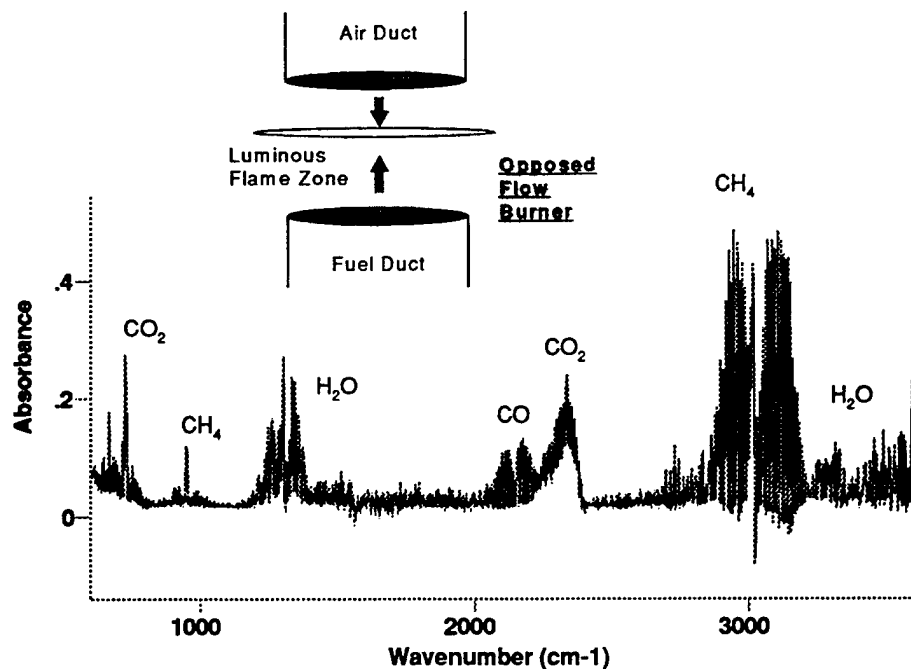
Figure 6. The IR Absorption Spectrum Measured Through a 50-Torr Opposed-Flow CH₄/Air Flame. The Inset Shows the Burner Configuration Used to Produce the Flame.
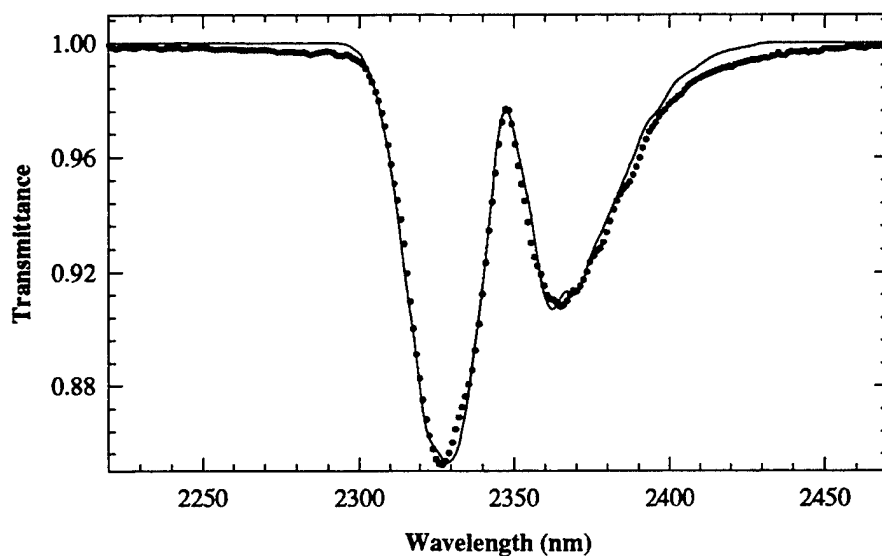

Figure 7. The Transmittance Spectrum of the First Overtone ($v = 0 - 2$) of CO. The Gas Was Contained in a Static Cell at 1 Atmosphere Total Pressure and a Temperature of 423 K. The Dotted Line Is the Measured Spectrum, and the Solid Line Represents the Least Squares Fit to the Data.

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A major difficulty in obtaining quantitative absorption measurements of flame species is that absorption of radiation by cold gases in the probe beam line of sight may lead to errors. Currently, several methods of excluding contributions to absorption by cold gases in the line of sight are used (Dasch 1992), with most methods employing some type of computer averaged tomography (CAT). Using these methods (often referred to as inversion methods), multiple line of sight measurements at different relative orientations are made within a plane, or slice, through the flame. Using these multiple line of sight measurements, numerical methods are used to calculate species concentration at a given point within the plane. Applying this technique to multiple planes, or slices, through the flame can yield a three-dimensional reconstruction of species concentration within the flame. This technique has been used to measure CO in reduced and atmospheric pressure flames (Best et al. 1991; McNesby et al. 1995). A summation of inversion methods used to measure temperatures and species in flames has been given by Limbaugh (1985).

It should be noted that, when measuring flame-absorption spectra using a FTIR spectrometer, care must be exercised so that flame emission is not reflected through the interferometer and reported as an absorption signal. To minimize the emitted radiation that reaches the interferometer, the collimated probe IR beam is brought to a focus at an iris prior to entering the flame region. After passing through the iris, the probe radiation is recollimated prior to entering the flame. While useful for identification of species within the flame, FTIR spectroscopy will not yield high spatial resolution unless the IR probe beam is reduced in cross section (usually by being passed through a set of apertures) prior to entering the flame region. This reduction in power of the IR probe beam energy reduces the signal-to-noise ratio in the measured spectrum. A typical experimental setup for measuring IR-absorption spectra through a flame using an FTIR spectrometer is shown in Figure 8.

Most commercial spectrometer systems employing broadband sources (typically FTIR systems) are not capable of resolving the true lineshape of an absorbing gas phase species because of limitations to instrument resolution. The instrument yields the convolution of the true absorbing gas lineshape and the instrument response function. Computer-based programs used to retrieve species concentration and temperature must either take into account this convolution

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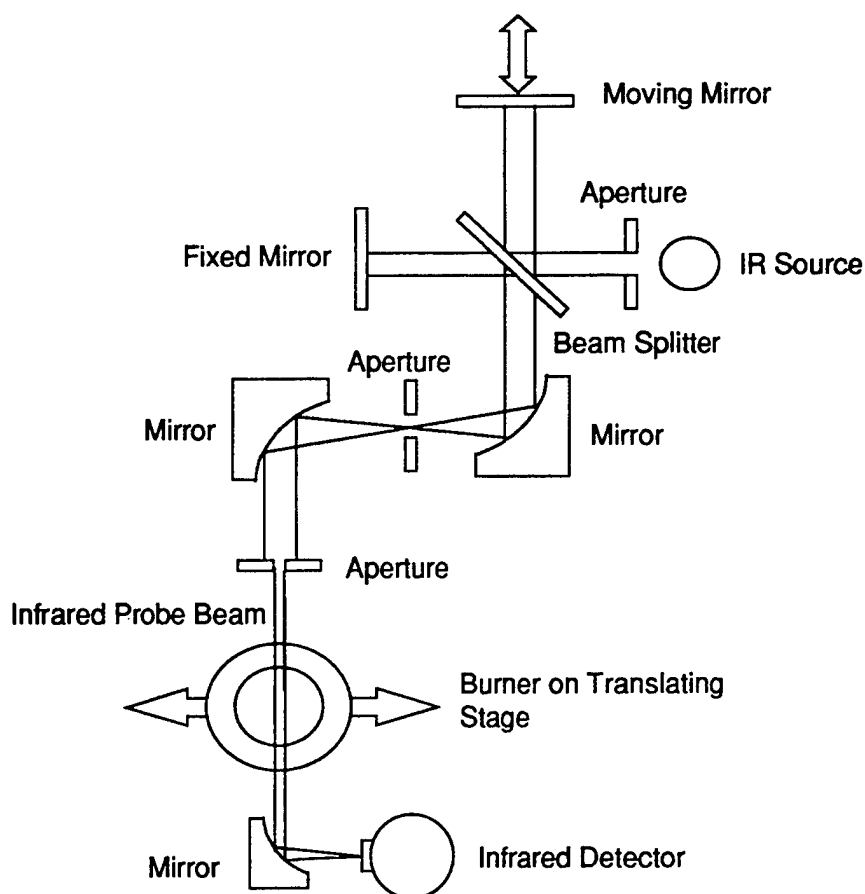
Figure 8. **Experimental Apparatus for Measurement of FTIR Absorption Spectra Through Flames. The System Is Designed to Minimize the Amount of Flame Emission That Reaches the Interferometer. The Burner Is Mounted on a Translating Stage (X and Z Axes) to Allow for Tomographic Analysis.**

or use for calculations the instrument response-corrected peak intensity of the rovibrational transition (Anderson and Griffiths 1975).

5. Experimental Methods - Applications of Tunable Diode Laser Absorption Spectroscopy (TDLAS)

TDLs are semiconductor devices (typically GaAs), which are essentially light-emitting diodes constructed within an optical resonator (Bomse et al. 1992). Lasing is achieved by delivering a small current to the photodiode. Tuning is achieved by changing the temperature

and, hence, the Fermi level of the device. The tuning range varies by type, but is usually between 2 cm^{-1} and 30 cm^{-1}. The useful tuning range (i.e., the range over which the device may be rapidly tuned without encountering changes in laser modes, which can mask absorption features) is usually less than 1 cm^{-1}. This restricted tuning range means that the devices are not used in a survey mode. In general, a TDL laser spectrometer system is designed to detect a single gas using a single, specially fabricated, dedicated, laser diode. Occasionally, absorption transitions from different gases of interest may occur within the useful tuning range of a single laser, but such occurrences are usually fortuitous. Additionally, because of the limited tuning range, calculation of temperature and species concentration may be difficult when only one line is measured.

There are, however, several advantages to using TDLs for measurement of gas phase flame species. These include high resolution (typically better than 1×10^{-4} cm^{-1}), good spatial resolution (200 μ to 1 mm), reasonable output power (~ 1 mW), and the ability to scan over their spectral range on a millisecond or better timescale. Probably, the most widely studied molecular flame species by TDL spectroscopy is CO. In addition to the reasons for study previously outlined in the discussion of broadband source methods, CO possesses several fundamental ($v = 0 - 1$) and hot-band transitions ($v = 1 - 2$, $v = 2 - 3$), which occur within several linewidths (approximately 0.05 cm^{-1}) of each other (Varghese and Hanson 1980). At room temperature, populations of states from which hotband transitions occur are very low. However, at flame temperatures, populations of vibrational states other than the $v = 0$ state may become appreciable. When temperatures (and also species concentrations) are calculated from simultaneous measurement of a fundamental and hotband transition, the technique is referred to as two-line thermometry (Hanson et al. 1980).

Figure 9 shows several spectra of CO measured in a low-pressure (20 torr), stoichiometric CH$_4$/O$_2$ flame using mid-IR TDL spectroscopy (Daniel et al. 1996). Because the wavelength of the diode laser radiation corresponds to single quantum number changes in CO (in this case, a $v = 0 - 1$ and a $v = 1 - 2$ transition) simple absorption spectroscopy may be employed. Each spectrum is measured at a different height above the burner surface. For these experiments, the
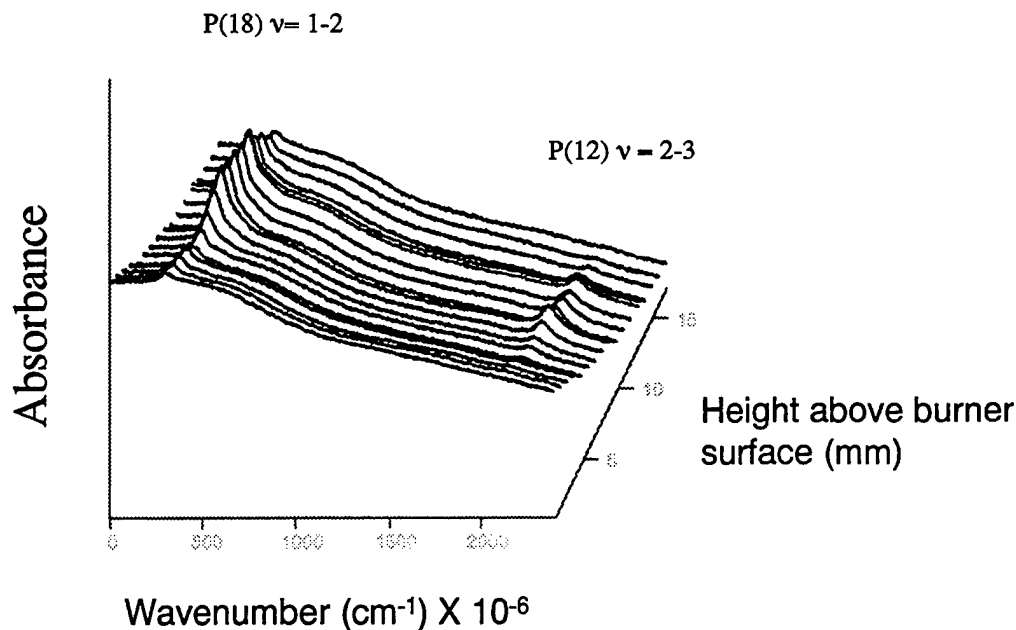
Figure 9. **Mid-IR TDL Spectra of CO, Measured Through a Premixed CH₄/O₂ Flame, at a Total Pressure of 20 Torr, as a Function of Height Above the Burner Surface. The Maximum Temperature Calculated Using Two-Line Thermometry Was 2,150 K.**

probe laser beam location was fixed and the burner location was translated vertically. The IR laser beam diameter through the flame region was 0.5 mm. As the diode laser radiation passes through different portions of the flame, the relative areas under the two peaks corresponding to absorption from different rovibrational levels changes. Figure 10 shows the results of fitting an equation similar to equation (19) to an absorption spectrum from Figure 9. Using this method, the CO vibrational temperature was calculated as a function of height above the burner surface (T_{max} = 2,150 K +/− 50 K). Additionally, tomographic analysis of the data showed that the error from cold gas absorption for these experiments was always less than 10% of calculated temperatures and partial pressures (McNesby et al. 1995).

TDL spectroscopy is also used for detection of many trace gas species in flames and in flame environments. The method used for measurements of small amounts of gases (often to the ppb range) relies on modulation spectroscopy using phase-sensitive detection. The principal advantage to using modulation spectroscopy results from minimization of laser output noise by
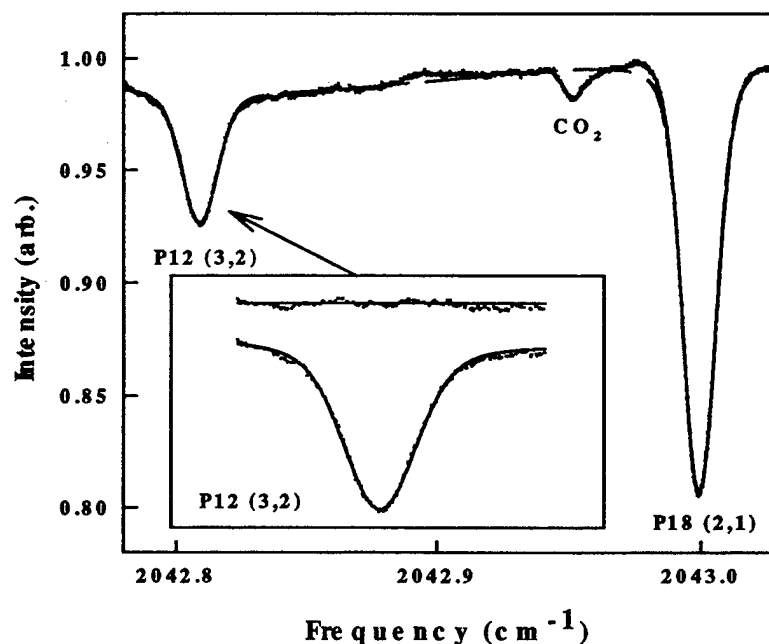
Figure 10. A Transmission Spectrum Measured Through a Low-Pressure, Premixed CH_4/O_2 Flame at 20 Torr. The Main Absorption Features Are the Two CO Lines Used to Calculate the Temperature Using the Method of Two-Line Thermometry. Calculated Temperature Was 2,150 K.

shifting detection to high frequencies (Bomse et al. 1992). When phase-sensitive detection is employed using TDLs, the second derivative of the diode laser probe beam intensity with respect to wavelength is usually measured, since the wavelength at which the second derivative is a maximum coincides with the wavelength of maximum light absorption. The second derivative signal peak height may be shown (Reid and Labrie 1981) to be proportional to absorbance, A:

$$. X''/ V = kA. \tag{20}$$

Here, X" is the peak height of the second derivative signal (volts), V is the direct-current (DC) voltage measured by the detector in the absence of any molecular absorbance, and k is a constant that includes the measuring instrument and optics function. Letting S, denoted as 2f signal peak height (peak to trough height, the distance between the maximum and minimum points on the 2f signal, see Figure 11[c]), equal X"/V, yields

$$S = (k\alpha) LP. \tag{21}$$

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2F DETECTION FOR TRACE GAS MEASUREMENT
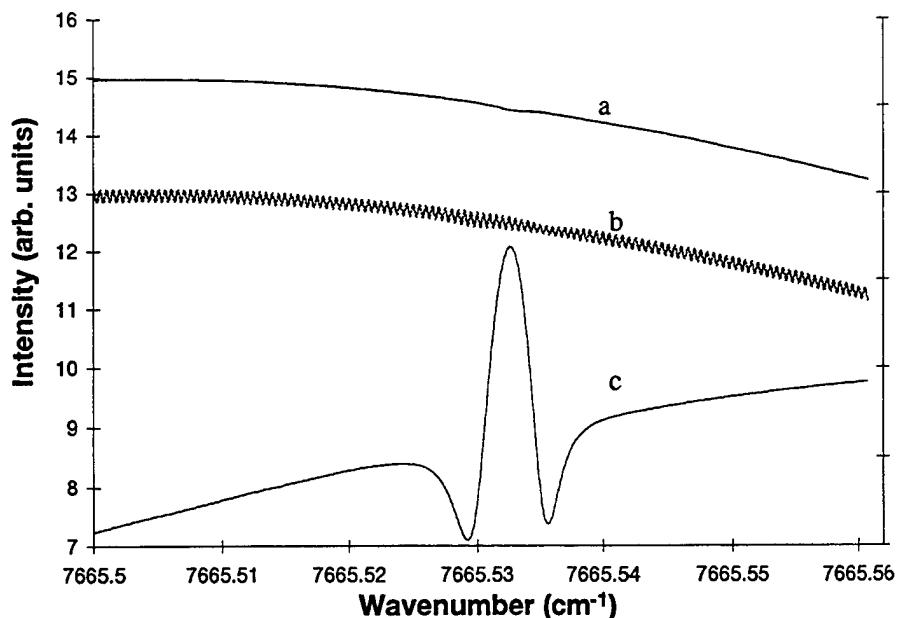
Figure 11. Simulated Signal vs. Wavelength of Laser Radiation After Passing Through a Gas With an Absorption Feature Near 7665.5 cm^{-1} Graphs for (a) Unmodulated Laser Radiation; (b) Laser Radiation With a Small-Amplitude, High-Frequency Modulation; and (c) Demodulation at Twice the High-Frequency Modulation in (b).

The slope of a plot of LP vs. S provides the value of kα. A calibration of the system using known concentrations of the absorbing gas must be performed to determine the value of kα. Once this value is known, gas pressure (P) may be obtained directly from equation (21). Care must be exercised so that changes in optical surfaces during measurement (as when measuring corrosive gases such as HF) do not affect the value of kα, since this value is instrument function dependent. For this reason, calibration should be performed at the beginning and end of each measurement set. Additionally, for gas concentrations that attenuate more than 5% of the incident light, the linear relationship between gas pressure and 2f Signal peak height may no longer hold (Miller et al. 1993).

Modulation spectroscopy using TDLs (often referred to as 2f spectroscopy) has been extensively discussed in the literature (Fried et al. 1998). Figure 11 gives a generic description

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of the signal processing employed in these experiments. Briefly, the laser output wavelength is scanned (10 Hz to 10 kHz) through a spectral region where the gas being measured absorbs. The output at the detector during the laser scan (with the high-frequency modulation turned off) may be seen in the upper trace of Figure 11. A high-frequency (10 kHz to MHz) wavelength modulation with an amplitude approximately equal to the linewidth under investigation is superimposed on the laser drive current (middle trace in Figure 11). Demodulation at twice the frequency of the high-frequency laser drive modulation yields the second derivative signal shown in the lower trace in Figure 11. It should be noted that the upper trace in Figure 11 shows that the laser diode output power has a nonlinear dependence on laser drive current. While this is nonideal behavior, this is a common trait of commercially available laser diodes. The nonlinear power output dependence on laser drive current (exaggerated here for illustration) causes the sloping baseline for the second derivative signal in Figure 11. For measurements at extremely low concentrations or for gases with small absorption cross sections, the nonlinearity of laser diode output power with laser drive current may affect limits of detection.

Modulation spectroscopy enables discrimination against contributions to light attenuation by scattering from particulate matter using a single laser beam. Attenuation of laser radiation by a rovibrational transition of a small gas molecule is detected because the wavelength range of the scan is several times the width of the spectral absorption feature (typically on the order of 0.1 cm^{-1} at atmospheric pressure). Because light scattering by particulate matter is nearly constant over the very small wavelength range of the laser scan, the change in detector signal intensity with the change in wavelength is effectively zero in the absence of any absorbing gas. However, because the 2f signal is also proportional to the background signal intensity, the second derivative signal is divided by the DC signal to account for light scattering by particles.

While modulation techniques enable trace gas detection, special care must be exercised when making measurements in flames, especially when using near-IR laser radiation. Significant errors in measured concentrations may arise because of beam steering as the laser radiation passes through the flame. In some cases, the beam steering may be severe enough to cause loss of signal at the detector. Secondly, great care must be exercised when measuring 2f spectra

through regions of differing temperature and pressure, since the 2f signal is extremely sensitive to changes in linewidth of the absorbing species (Reid and Labrie 1981).

6. Conclusion

IR spectroscopy continues to be a valuable tool for measuring species concentrations and temperatures in flames and combustion gases, especially in field-based studies. The advent of compact, fiber-coupled TDLs operating at room temperature is expanding the use of vibrational spectroscopy beyond the laboratory and providing a useful complement to broadband methods currently in place.

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An overview of the application of vibrational spectroscopy to the study of flames is provided. The mathematics of interpretation of flame spectra for determination of species concentration and temperature are introduced. The history of the application of vibrational spectroscopy to the study of flames is briefly summarized. Applications of methods using dispersive absorption and emission spectroscopy and of methods using tunable diode lasers (TDLs) to the study of flame systems are discussed.

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